

OSCILLATOR STRENGTHS FOR THE $X^1\Sigma^+-A^1\Pi$ SYSTEM OF CH^+

M. YOSHIMINE

IBM Research Laboratory, San Jose, California

AND

S. GREEN* AND P. THADDEUS

Goddard Institute for Space Studies, New York City

Received 1973 February 1

ABSTRACT

Oscillator strengths for the $X^1\Sigma^+-A^1\Pi$ system of CH^+ have been computed to an estimated accuracy of 10 percent from *ab initio* wave functions. The $f_{v'v''}$ values for the two strongest interstellar lines, $\lambda\lambda 4232$ and 3957 , are found to be, respectively, $f_{00} = 6.45 \times 10^{-3}$ and $f_{10} = 4.31 \times 10^{-3}$.

Subject headings: interstellar matter — molecules — transition probabilities

Although CH^+ was one of the first molecules detected in the interstellar medium, its abundance has remained uncertain because oscillator strengths for the observed transitions, members of the $X-A$ electronic system, are not accurately known (see, e.g., Herbig 1968). Knowledge of these is also required to assess the two-body radiative association mechanism proposed for the formation of this molecule in space (Bates and Spitzer 1951; Solomon and Klemperer 1972). Because it is both charged and highly reactive, CH^+ is difficult to study in the laboratory. Smith (1971) has obtained a lifetime measurement for the A state, but his experiment suffers from incomplete spectral resolution and other difficulties, and the value which he derives for the electronic oscillator strength of the $X-A$ system, $f_{e1} = 0.072$, is surprisingly large when compared to known values for similar molecular transitions. Lutz (1972), for example, has pointed out that in terms of the known f_{e1} of the same systems of CH , SiH , and SiH^+ one may estimate the CH^+ oscillator strength to be $f_{e1}(\text{CH}^+) \approx f_{e1}(\text{CH})f_{e1}(\text{SiH}^+)/f_{e1}(\text{SiH}) \approx 0.11$ —only one-sixth of the value obtained by Smith.

Ab initio quantum-mechanical calculations of molecular structure, on the other hand, are now so accurate that some parameters of simple molecules can be predicted more accurately than they can be measured, particularly for unstable molecules. In this article we give oscillator strengths for the $X-A$ CH^+ system obtained from such a calculation which are probably good to 10 percent, and which yield for f_{e1} a value significantly lower than that obtained by Smith, but in good agreement with Lutz's estimate.

The oscillator strength is given by (see, e.g., Liu *et al.* 1973)

$$f_{v'v''} = \frac{2}{3}g\Delta E \left[\int dr dR \Psi_{\alpha'v'}^*(r, R) r \Psi_{\alpha''v''}(r, R) \right]^2, \quad (1)$$

where ΔE is the transition energy, g is a degeneracy factor equal to 2 for this system, and $\alpha'v'$ and $\alpha''v''$ are electronic and vibrational quantum numbers for the upper and lower levels, respectively; all quantities are in atomic units. The wave functions Ψ are solutions of the nonrelativistic Schrödinger equation, and depend on the inter-

* National Research Council Resident Research Associate supported by the National Aeronautics and Space Administration.

nuclear distance R as well as on the electronic coordinates r . With the usual Born-Oppenheimer approximation of separate nuclear and electronic motions, Ψ_{av} is the product of vibrational and electronic functions

$$\Psi_{av}(r, R) = \Psi_v(R)\Psi_a(r, R); \quad (2)$$

and equation (1) becomes

$$f_{v'v''} = \frac{2}{3}g\Delta E \left[\int dR \Psi_{v'}^*(R) M(R) \Psi_{v''}(R) \right]^2, \quad (3)$$

where the electronic transition moment is

$$M(R) = \int dr \Psi_a^*(r, R) r \Psi_a(r, R), \quad (4)$$

whose only nonvanishing component (in spherical tensor notation) is

$$M_+(R) = \int dr \Psi_{\pi}^*(r, R) [2^{-1/2}(x + iy)] \Psi_{\Sigma}(r, R). \quad (5)$$

It is commonly assumed that $M(R)$ is a constant M over the vibrational motion, so the oscillator strengths for different vibrational transitions are simply

$$f_{v'v''} = \frac{2}{3}g\Delta E M^2 q_{v'v''} = f_{el} q_{v'v''}, \quad (6)$$

and thus proportional to the Franck-Condon factors

$$q_{v'v''} = \left[\int dR \Psi_{v'}^*(R) \Psi_{v''}(R) \right]^2. \quad (7)$$

This approximation has not been made in the present study and, as will be seen, it holds rather poorly for CH^+ .

The Ψ used in our calculation are among the most accurate molecular wave functions obtained to date (Green *et al.* 1972); they yield values for the CH^+ equilibrium internuclear distances and vibrational frequencies which are in excellent agreement with experiment, and potential curves computed from them have been instrumental in correcting an error in previously reported Franck-Condon factors for the $X-A$ system (Liszt and Smith 1972; Green *et al.* 1973).

The electronic transition moment computed from equation (5) as a function of internuclear distance is given in table 1. Based on the accuracy obtained in comparable atomic calculations (Schiff and Pekeris 1964; Weiss 1967; Westhaus and Sinanoğlu 1969), and on the knowledge that diagonal molecular dipole moments are obtained to within 1 percent with similar wave functions, the values in table 1 are estimated to be within 10 percent of the exact nonrelativistic, Born-Oppenheimer values. It can be seen that the calculated transition moment vanishes, as it should, in the separated-atom limit (it should also vanish in the united-atom limit, but at 1.5 atomic units—the smallest separation at which calculations were done—the molecule is expected to be still quite far from this limit). Band oscillator strengths $f_{v'v''}$ for vibrational transitions of interest have been obtained by solving equation (3); results are presented in table 2. Because $M(R)$ is found to vary significantly with R , $f_{v'v''}/q_{v'v''}$ in table 2 is not independent of the vibrational quantum numbers, and accordingly equation (6) is a rather poor approximation for the $X-A$ system.

It is interesting finally to note that astrophysical data also show that equation (6) is incorrect and lend further support to the accuracy of our calculations. The two

TABLE 1
X-A TRANSITION MOMENT AS A FUNCTION OF
INTERNUCLEAR DISTANCE (atomic units)

R	$M_+(R)$	$\frac{2}{3}g\Delta E(R)M_+^2(R)$
1.5.....	0.463	0.0368
1.75.....	0.412	0.0282
2.0.....	0.353	0.0198
2.5.....	0.190	0.0048
3.0.....	0.040	0.0002
4.0.....	0.001	0.0000
5.0.....	0.001	...
8.0.....	0.001	...

TABLE 2
BAND-OSCILLATOR STRENGTHS FOR THE X-A SYSTEM

$v'(^1\Pi)$	$v''(^1\Sigma^+)$	$f_{v'v''}$	$f_{v'v''}/q_{v'v''}$
0.....	0	0.00645	0.010
1.....	0	0.00431	0.016
2.....	0	0.00173	0.024
0.....	1	0.00097	0.003
1.....	1	0.00110	0.008
2.....	1	0.00306	0.012

strongest interstellar lines of CH^+ are $\lambda\lambda 4232$ and 3957 , the $R(0)$ lines of the $0-0$ and $1-0$ bands, respectively. In the best-studied interstellar cloud with CH^+ , that in front of ζ Oph, the equivalent widths of these lines are respectively 24.3 and 14.8 mÅ (Bortolot, Shulman, and Thaddeus 1973). Neglecting saturation entirely, one then obtains as an upper limit to the ratio of oscillator strengths

$$\frac{f_{10}}{f_{00}} \leq \frac{\lambda(4232)W(3957)}{\lambda(3957)W(4232)} = 0.65, \quad (8)$$

which is in excellent agreement with the theoretical value 0.67 obtained from table 2. Saturation is unlikely to affect this result significantly. Hobbs (1972) has recently resolved $\lambda 4232$ in ζ Oph, and finds its full width at half-maximum to be about 62 mÅ. When this is entered into the usual curve of growth for Doppler-broadened lines, it is found that the optical depths in the line centers are $\tau(4232) = 0.441$ and $\tau(3957) = 0.252$. The ratio of oscillator strengths corrected for saturation then becomes

$$\frac{f_{10}}{f_{00}} = \frac{\lambda(4232)\tau(3957)}{\lambda(3957)\tau(4232)} = 0.61. \quad (9)$$

In view of the observational uncertainties this can be considered as being in excellent agreement with the *ab initio* quantum-mechanical calculation.

REFERENCES

- Bates, D. R., and Spitzer, L. 1951, *Ap. J.*, **113**, 441.
 Bortolot, V. J., Shulman, S., and Thaddeus, P. 1973, in preparation.
 Green, S., Bagus, P. S., Liu, B., McLean, A. D., and Yoshimine, M. 1972, *Phys. Rev. A*, **5**, 1614.
 Green, S., Hornstein, S., and Bender, C. F. 1973, *Ap. J.*, **179**, 671.
 Herbig, G. H. 1968, *Zs. f. Ap.*, **68**, 243.
 Hobbs, L. H. 1972, *Ap. J. (Letters)*, **175**, L39.

- Liszt, H. S., and Smith, W. H. 1972, *J. Quant. Spectrosc. and Rad. Transf.*, **12**, 947, 1591.
Liu, B., McLean, A. D., and Yoshimine, M. 1973, *J. Chem. Phys.*, to be published.
Lutz, B. L. 1972, private communication.
Schiff, B., and Pekeris, C. L. 1964, *Phys. Rev.*, **134**, A638.
Solomon, P. M., and Klemperer, W. 1972, *Ap. J.*, **178**, 389.
Smith, W. H. 1971, *J. Chem. Phys.*, **54**, 1384.
Weiss, A. W. 1967, *Phys. Rev.*, **162**, 71.
Westhaus, P., and Sinanoğlu, O. 1969, *Phys. Rev.*, **183**, 56.